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Exocrine Secretions of Scentless Plant Bugs: *Jadera*, *Boisea* and *Niesthrea* species (Hemiptera: Heteroptera: Rhopalidae)

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Key Word Index—Serinethinae; Rhopalinae; Sapindaceae; Aceraceae; (*E*)-2-hexenal; monoterpene; 2-phenylethanol; 5-hydroxy-4-decanolide; allomone; scent gland; predation.

Abstract—The so-called scentless plant bugs are actually exceptionally redolent insects. Twenty-two volatile exocrine compounds were identified from eight rhopalid species, including monoterpene hydrocarbons and alcohols, alkenals and ketoalkenals, 2-phenylethanol and (4*S*,5*S*)-(+)-5-hydroxy-4-decanolide. The lack of species-specificity for the exocrine blends from eastern and western boxelder bugs (*Boisea trivittatus* and *B. rubrolineatus*, respectively) cast doubt on their validity as separate species. The biological roles for the array of exocrines released by rhopalids are largely unknown, but potentially important because boxelder bugs are an increasing urban nuisance and species such as *Niesthrea louisianica* may be useful weed control agents.

Introduction

Scentless plant bugs are medium-sized seed predators, some of which are of economic significance, either because of their pest status [e.g. the boxelder bug, *Boisea trivittatus* (Say)] [1] or because of their potential as weed control agents (e.g. *Niesthrea louisianica* Sailer) [2, 3]. Despite the epithet "scentless plant bugs", rhopalids are remarkable natural product chemists [4, 5]. The term scentless plant bug is completely inappropriate for Rhopalinae because species of this subfamily have the metathoracic scent gland common to other adult heteropterans [5], plus they retain the anterior dorsal abdominal gland usually found only in immature bugs [4]. Members of the only other subfamily in the group, the Serinethinae, have in fact largely lost the capability of *de novo* chemical fortification, evidently due to specialization on poisonous plants from which the bugs sequester toxins [6, 7]. Nevertheless, adult serinethines retain a pair of dorsal abdominal scent glands [4]. In addition, adult males of both rhopalid subfamilies excrete fragrant secretions from a gland associated with the genitalia [5, 8]. The present communication reports on the composite exocrine chemistry of eight species of rhopalids. Our results have taxonomic implications for *Boisea* (formerly *Leptocoris* [9]) and provide an insight into the chemical vocabulary of these semisocial bugs.

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Results

Insects and host plants

The Nearctic boxelder bug, *B. trivittatus*, was collected on pistillate boxelder trees, *Acer negundo* L. (Sapindales: Aceraceae), during late summer and early fall, 1985 and 1986, in Maryland and Utah. Boxelder bugs typically move from the pistillate racemes late in the season and gradually aggregate in nearby areas receiving direct insolation [1, 10]. In Maryland in 1985 this occurred during the third week in September. On 22 September, *ca* 1000, late fifth instar larvae and teneral adults were collected from an aggregation of at least 10,000 bugs on the trunk of a pistillate boxelder tree and an adjacent sunlit brick wall. Aggregations near host trees eventually disperse after periods of freezing temperatures as the cuticle of teneral adults hardens and they are able to fly to overwintering sites, often in or near buildings, where they reaggregate [1, 11]. A significant excess of *B. trivittatus* females (64%, $n=113$, $\chi^2=8.5$, $P<0.005$) was collected near host trees in Maryland on 7 October 1986, after most bugs had migrated.

The other Nearctic *Boisea* species, *B. rubrolineatus* Barber, feeds on boxelder (S.P. Carroll, personal observation) and big-leaf maple, *Acer macrophyllum* Pursh. [10, 12]. *Boisea rubrolineatus* adults were collected from racemes of a big-leaf maple in California, on 22 June 1986.

All *Jadera* species were collected by S.P.C. and express-mailed to J.R.A. for dissection or rearing. In 1985, larvae and adults of *J. haematoloma* (Herrick–Schaeffer) were collected at several locations and on different species of Sapindaceae as follows: Florida, on *Koelreuteria paniculata* (golden rain tree) (May); Florida, on *Cardiospermum corindum* (balloon vine) (December); Arizona, on *Sapindus drummondii* (soapberry) (October); Oklahoma, on *S. drummondii* (October); Oklahoma, on *K. paniculata* (golden rain tree) (October); and Oklahoma, on *S. drummondii* (October). *Jadera haematoloma* reported by J.R.A. to feed on short-leaved fig, *Ficus brevifolia* (Moraceae) [4], were probably feeding on seeds of balloon vines entangling or nearby the fig tree. *Jadera sanguinolenta* (F.) were collected in Florida on *K. paniculata* (December). The *Koelreuteria* species is introduced; balloon vine and soapberry are native hosts [12]. Cultures of *J. haematoloma* and *J. sanguinolenta* were maintained on *K. paniculata* seeds for several generations and for one generation on *C. corindum* and *C. grandiflorum* seeds, plus water. A few adults of *J. antica* were collected on *C. corindum* in Florida, a single adult male *J. obscura* was collected on *Thinouia decapleuria* (Sapindaceae) in Panama, in April 1985, and a single adult male *J. hinnulea* was collected on *Serjania brachycarpa* (Sapindaceae) in Texas, in January 1989.

Niesthrea louisianica adults were obtained from a laboratory colony originating near Stoneville, Mississippi, from specimens collected on velvetleaf, *Abutilon theophrasti* Medic. (Malvaceae), a major exotic weed of row crops in much of the United States [2, 3]. In addition, a group of *ca* 200 adults was field collected on rose of Sharon, *Hibiscus syriacus* L. (Malvaceae), in Georgia, in July 1987.

Exocrine glands and chemistry

The adult *Jadera* and *Boisea* species that we studied had only vestiges of the metathoracic scent glands common to other Heteroptera. The larvae have two dorsal abdominal glands (DAGs) opening between the fourth–fifth and fifth–sixth segments, as often found in immature heteropterans, but the openings of these glands are much closer together than in other bugs [13]. In the *Boisea* species, the anterior DAG is flaccid and empty after the molt to the adult stadium, but the posterior DAG remains functional and appears identical to that of larvae. In *Jadera*, both the anterior and posterior DAGs are retained as active glands in adults. In addition, males possess a small ventral abdominal gland (VAG) opening medially between the last abdominal segment and the first genital segment [5, 8].

In an earlier study of *J. haematoloma*, (*E*)-2-hexenal and (*E*)-2-octenal plus four monoterpene hydrocarbons were identified, but only adults were investigated and the DAGs were extracted together [4]. From the present study it is clear that in species of *Jadera* the unsaturated carbonyl compounds are produced exclusively in the anterior DAG (Fig. 1), whereas the monoterpene hydrocarbons are unique to the posterior DAG (Fig. 2). Furthermore, the VAGs of

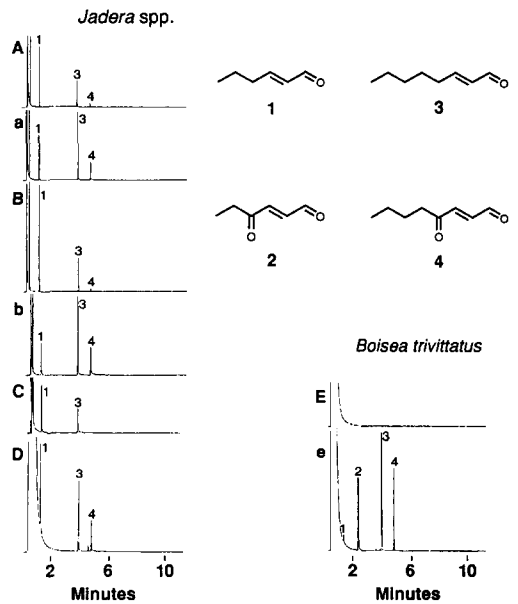

FIG. 1. GAS CHROMATOGRAMS OF CH_2Cl_2 EXTRACTS OF ANTERIOR DORSAL ABDOMINAL GLANDS FROM *JADERA* AND *BOISEA*: (A) *J. haematoloma* adults; (a) *J. haematoloma* larvae; (B) *J. sanguinolenta* adults; (b) *J. sanguinolenta* larvae; (C) *J. obscura* adult; (D) *J. antica* adults; (E) *B. trivittatus* adults; (e) *B. trivittatus* larvae.

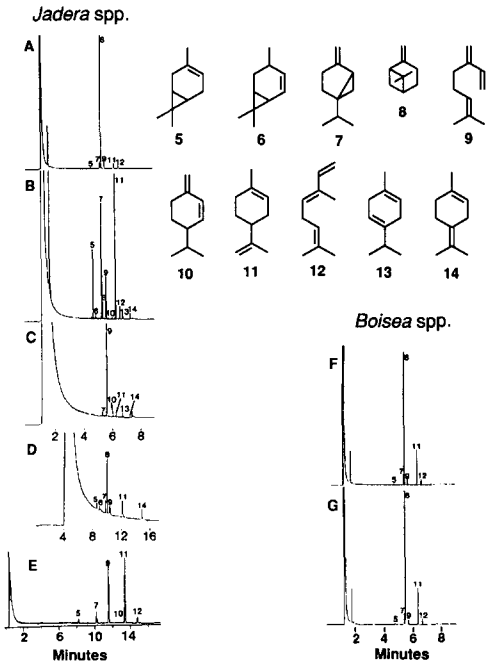

FIG. 2. GAS CHROMATOGRAMS OF CH_2Cl_2 EXTRACTS OF POSTERIOR DORSAL ABDOMINAL GLANDS FROM ADULT *BOISEA* AND *JADERA*: (A) *J. haematoloma*; (B) *J. sanguinolenta*; (C) *J. obscura*; (D) *J. antica* (60 m DB-1 column); (E) *J. hinnulea* (reconstructed ion chromatogram from GC-MS); (F) *B. trivittatus*; (G) *B. rubrolineatus*.

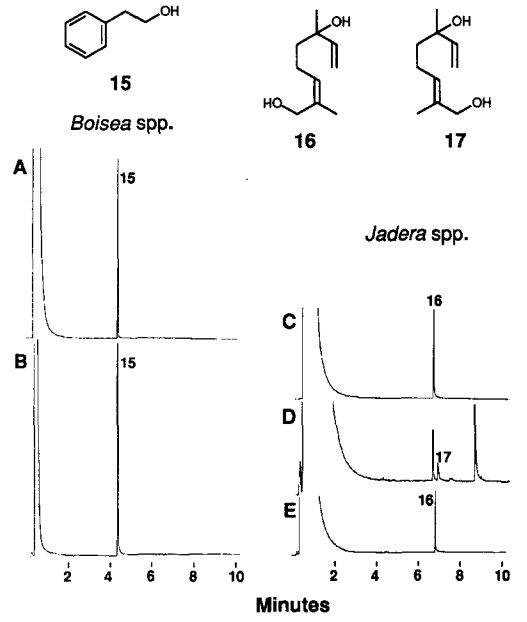

FIG. 3. GAS CHROMATOGRAMS OF CH_2Cl_2 EXTRACTS OF VENTRAL ABDOMINAL GLANDS FROM MALE *JADERA* AND *BOISEA*: (A) *B. trivittatus*; (B) *B. rubrolineatus*; (C) *J. haematoloma*; (D) *J. sanguinolenta*; (E) *J. obscura*.

Jadera spp. produce hydroxylated compounds not found in either DAG (Fig. 3).

The anterior DAG secretions of *Jadera* are dominated by α,β-unsaturated aldehydes **1** and **3**, with lesser amounts of keto-aldehyde **4** (Fig. 1A–D). In boxelder bug adults this gland is empty (Fig. 1E). In larvae the gland is active, but keto-aldehyde **2** replaces the 6-carbon aldehyde **1** as a major constituent of the secretion, and compounds **4** and **3** are major components (Fig. 1e). Anterior DAG secretions are not species-specific, but comparison of the secretions of larvae to those of adults for *J. haematoloma* and *J. sanguinolenta* shows that the larval secretions (Fig. 1a, b) contain relatively more of the higher molecular weight components **3** and **4** than do the adult secretions (Fig. 1A, B). The compositions of anterior DAG secretions were nearly identical for field-collected *J. haematoloma* males and females from Florida, Oklahoma and Arizona, regardless of host plant; the percentages ($X\pm$S.E.M.) of compounds **1**, **3** and **4**, respectively, were 70.4±2.1, 26.0±1.7 and 3.6±0.5 for males ($n=7$), and 70.9±1.3, 24.7±1.5 and 4.5±0.9 for females ($n=5$). Field-collected larvae from Florida and Arizona produced anterior DAG secretions containing 36.6±4.6, 54.0±2.9 and 9.4±3.3 (%X+S.E.M., $n=3$) of compounds **1**, **3** and **4**, respectively.

The posterior DAG secretions of *Boisea* and *Jadera* are composed exclusively of monoterpene hydrocarbons. In *Jadera*, these secretions are quantitatively species-specific (Fig. 2); most of the same monoterpenes (**5**–**14**) occur in the posterior DAG exudates, but in vastly differing amounts between species (Fig. 2A–E). In contrast, the posterior DAGs of *B. trivittatus* and *B. rubrolineatus* produce secretions that are virtually identical (Fig. 2F, G). For *J. haematoloma*, *J. sanguinolenta* and *B. trivittatus*, extracts of the posterior DAGs were analysed separately for males, females and larvae. Within a species these extracts were indistinguishable by gas chromatography. Additionally, in *J. haematoloma* the composition of the posterior DAG secretion was constant regardless of collection locale or host plant, and regardless of whether the insects

were reared under long-day conditions (16:8 h L:D) or a short-day regime (10:14 h L:D).

A third set of chemically distinctive volatile exocrines is produced in the male-specific VAG of Serinethinae (Fig. 3). The VAG secretions of *B. trivittatus* and *B. rubrolineatus* are the same; each species produces practically pure 2-phenylethanol (**15**) (Fig. 3A, B). Male boxelder bugs collected during February in Utah from hibernating aggregations produced little or no compound **15**. In *Jadera*, the VAG secretions of the sympatric species, *J. haematoloma* and *J. sanguinolenta*, are qualitatively distinctive, while the allopatric *J. obscura* males produce nearly pure compound **16**, as do *J. haematoloma* males (Fig. 3C–E). For *J. haematoloma* and *J. sanguinolenta*, the VAGs from 30 or more males were required to detect volatiles, but the VAG extract of the single *J. obscura* male obtained from Panama was sufficient to detect *cis*-8-hydroxylinalool (**16**), The meager amounts of material available from *J. sanguinolenta* VAGs precluded identification of the components eluting before and after *trans*-8-hydroxylinalool (**17**).

The exocrine chemistry of the rhopaline, *Niesthrea louisianica*, is simultaneously alike and unlike that of serinethines (Fig. 4). As in the Serinethinae, the larval anterior DAG secretion is dominated by an α,β-unsaturated alkenal (**1**) and a 4-keto-2-alkenal (**2**), while the posterior DAG secretion contains a mixture of monoterpene hydrocarbons (**8**, **9**, **11** and **14**). However, the anterior DAG secretion of *Niesthrea* larvae also contains a monoterpenol (perilla alcohol, **18**) and limonene (**11**), although the latter compound may be a contaminant from the posterior DAG secretion. Keto-alkenal **2** is absent from the anterior DAG secretion of *N. louisianica* adults, similar to serinethines where this secretion is relatively less volatile in adults than larvae, but the greater abundance of compound **18** in the secretion is contrary to this trend. The posterior DAG is inactive in *N. louisianica* adults, yet the metathoracic scent gland secretion contains the same monoterpenes (**8**, **11** and **14**) as produced in the larval posterior DAG, along with the predominant component, thymol (**19**) [4]. Finally, the VAG secretion of *Niesthrea* males resembles those of *Jadera* males in that monoterpenols (**20** and **21**) are present. Nevertheless, the major VAG secretory component of *Niesthrea* males,

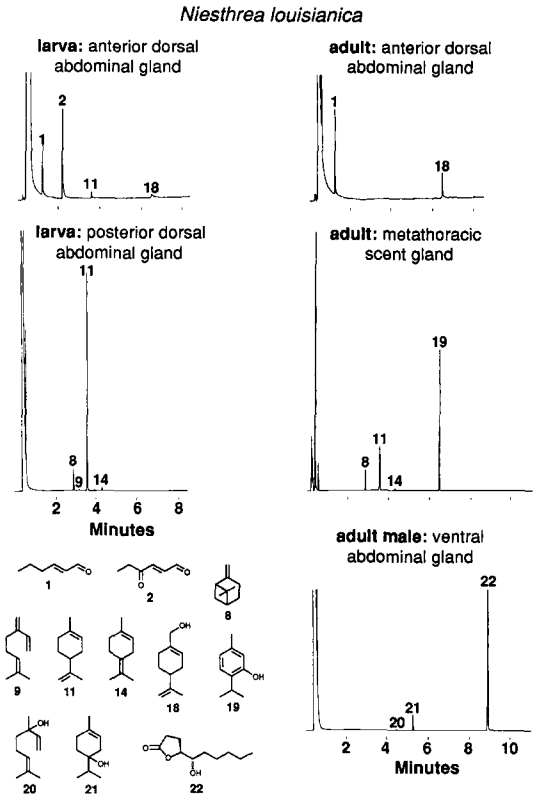

FIG. 4. GAS CHROMATOGRAMS OF CH_2Cl_2 EXTRACTS OF *NIESTHREA* EXOCRINE GLANDS.

(4*S*, 5*S*)-5-hydroxy-4-decanolide (**22**), is unprecedented among the Heteroptera [5].

Alarm pheromone bioassay

(*E*)-2-Hexenal (**1**), (*E*)-2-octenal (**3**) and racemic β-pinene (**8**) were tested for alarm-releasing activity with *J. haematoloma* larvae after the method of Moser *et al.* [14]. Groups of *ca* 15 fifth instar larvae were coaxed into a 40×4 cm glass column containing a water bottle and five *K. paniculata* seeds. The column ends were closed with porous glass stopcocks, one of which was connected via a flow-control valve to the house vacuum (25 ml min^{-1}), the other was connected via a short piece of silicone tubing to ambient air drawn through a charcoal filter and bubbled through water. For testing, 0.25, 2.5, 5, 10 or 50 ml of saturated vapor of the test compound were drawn from the headspace of a 250-ml flask containing the compound into a gas-tight

syringe and injected into the upwind end of the apparatus through the silicone tubing. Equal volumes of ambient air were injected between test compound injections and a minimum of 15 min was allowed to elapse before injection of the next higher concentration of test compound(s). Different groups of fifth instars were subjected to concentration series of (*E*)-2-hexenal, (*E*)-2-octenal, (±)-β-pinene and (*E*)-2-octenal/(±)-β-pinene (1:1 by volume); second and third instars were tested with (*E*)-2-octenal and (±)-β-pinene series.

The results of these tests were not dramatic. Even at the highest concentrations of test compounds (10^{16}–10^{17} molecules ml^{-1}) the bugs often continued feeding and, at most, showed only moderately increased movement and grooming. It is noteworthy that these bugs can always be induced to run frantically merely by gently tapping on their rearing dishes. No such response was ever induced by exposure to the major DAG components. At best, insects exposed to DAG components were more alert to physical disturbance than untreated larvae.

Discussion

Scentless plant bugs are exceptionally redolent insects, especially the Rhopalinae which retain the metathoracic scent gland characteristic of other true bugs. In Serinethinae the loss of the metathoracic scent gland stems from an ancient association with poisonous plants; serinethines are gregarious, vividly marked, red insects that suck the seed oil of toxic Sapindales, especially Sapindaceae containing cyanolipids [15, 16]. Serinethines specializing on sapindaceous hosts sequester the cyanide-containing moieties in their blood as glucosides and readily bleed when attacked [7, 17], thereby rendering themselves unpalatable to a variety of predators [18]. Thus, the chemical ecology of Serinethinae is analogous to that of seed bugs in the subfamily Lygaeinae (Lygaeidae), where aposematism and sequestration of cardiac glycosides evolved with Apocynales seed predation [19]. *Niesthrea louisianica* feeds only on seeds of malvaceous plants, including exotic species such as cotton, *Gossypium hirsutum* L. and velvetleaf *Abutilon theophrasti* Medic. [20, 21]. Whether appropriation of toxins is part of the defensive *modus operandi* of *Niesthrea* is unknown.

Clustered *Jadera* will emit a scent when gently exhaled upon and rapidly retreat, and diapausing clumps of adult *J. haematoloma* so disturbed react with much greater alacrity than when manually disturbed (Carrol, S. P., personal observation). Even so, fifth instar *J. haematoloma* were not alarmed by high concentrations of alkenals **1** and **3**, and/or β-pinene (**8**). Besides the intrinsic irritancy to predators of alkenal, keto-alkenal and monoterpene vapors, scent gland odors may also serve as aposematic signals associated with blood-borne toxins, particularly for color-blind predators that hunt by scent like shrews (Insectivora) [22]. The anterior DAG secretions of serinethines are compositionally noteworthy for the enrichment of lower molecular weight components in larvae, presumably because the flightless immatures require longer lasting protection [5]. Serinethine posterior DAG secretions consist entirely of monoterpene hydrocarbons and, in *Jadera*, these secretory blends are highly species-specific. Larvae of a shield bug, *Hotea gambiae* (Westwood) (Scutelleridae), secrete a mixture of isoprenoids from a pair of DAGs [23], but in adults the glands produce almost pure (*E*)-2-hexenol [24]. Swallowtail butterfly larvae (Lepidoptera: Papilionidae) have an eversible osmetrium whose secretion includes many of the same monoterpenes identified from *Jadera*, but these osmeterial secretions show remarkable differences between larval stages and between individuals within a stage [25]. *Jadera* terpene blends are virtually constant for a species regardless of diet, stadium, sex, or geographic origin. The intraspecific uniformity and species-specificity of the posterior DAG secretions of *Jadera* suggest they play some kind of pheromonal role, perhaps involving species recognition and aggregation.

The precise role of VAG secretions in Heteroptera also remains speculative, but it is clear that the sympatric species, *J. haematoloma* and *J. sanguinolenta*, produce distinctly different VAG secretions. Similarly, seven species of leaf-footed bugs in the genus *Leptoglossus* (Coreidae) each produce a unique VAG secretion [26, 27]. Therefore, the demonstration that the VAG secretions of *B. trivittatus* and *B. rubrolineatus* are identical is anomalous. Furthermore, the two boxelder bug species produce identical posterior DAG secretions, while those of *Jadera* are

species-specific. These chemical data cast doubt on the validity of *B. trivittatus* and *B. rubrolineatus* as separate species, especially since they are separable only by color-pattern [28].

Aggregations of *Jadera* often have more males than females resulting in intense competition for mates [16, 29, 30]. Copulation lasts much longer than necessary for sperm transfer in *N. louisianica* [20] and serinethines [29] and, at least in *J. haematoloma*, males further ensure paternity by guarding their mate while she lays eggs [29]. It is in this context that the male-specific VAG bouquets probably play a part. The *Boisea* VAG component, 2-phenylethanol (**15**), is one of the most common of the compounds administered to female moths from the hair-pencils and scent brushes of courting males [31]. Linalool is widespread in heteropteran secretions [5], but the discovery of 8-hydroxylinalool isomers in the VAG secretions of *Jadera* is the first occurrence of these compounds outside the plant kingdom. In *N. louisianica* the VAG is considerably larger than in males of serinethine species. The major product of this species' VAG is (4*S*,5*S*)-5-hydroxy-4-decanolide (**22**), a compound heretofore known only from the bacterium, *Streptomyces griseus* [32, 33]. The possibility that **22** is biosynthetised by a symbiotic *Streptomyces* bacterium must be considered in view of the propensity of Heteroptera to harbor microbial symbionts [34] and the likelihood that lactonic exocrine secretions in some insects are produced by symbiotic microorganisms [35, 36].

When rhopalids and coreids copulate, secretion oozes from the male's VAG, suggesting that these "perfumes" somehow stimulate or mark females. These exudates may also be signals in male–male encounters. For example, in aggregations of *J. haematoloma*, males are mounted by other courting males but are quickly rejected after the courting male antennates the genitalia of his partner [29].

Further research is needed to elucidate the behavioral roles for the bewildering array of semiochemicals emitted by "scentless plant bugs". For *N. louisianica* the prospect of deciphering the pheromonal roles of exocrines has practical implications because augmentation of the bug in velvetleaf-infested fields significantly reduces the seed viability of this important weed [37, 38].

Experimental

Exocrine glands were dissected separately from bugs anesthetized with CO_2 and immersed in tap water. Usually three to seven glands were macerated in *ca* 100 µl of CH_2Cl_2 (Burdick and Jackson). Concentrated extracts of fewer or more glands were prepared for some species. Analytical gas chromatography (GC) was performed using a Varian 3700 GC with a Shimadzu C-R3A recorder, on bonded methyl silicone capillary column (0.25 mm i.d.; D.B.-1™, J&W Scientific, Folsom, CA) with helium as carrier (40 cm s^{-1}). Posterior DAG extracts were run on 30 m DB-1 (60°C for 10 min to 240°C at 25°C min^{-1}) and 60 m DB-1 (90°C for 14 min to 190°C at 25°C min^{-1}) columns. Other extracts were run on a 15 m DB-1 analytical column (anterior DAG and VAG: 45°C for 2 min to 230°C at 15°C min^{-1}). Compound **22** was isolated in a glass capillary tube as it eluted from a DB-1 column (15 m × 0.53 mm i.d.) in a Varian 3700 GC equipped with a thermal conductivity detector. GC-mass spectrometry was conducted using a Finnigan 4510 GC-MS system on a 30 m DB-1 column. ^1H NMR spectra were recorded at 300 and 500 MHz on General Electric QE-300 and GN-500 instruments, respectively, with TMS as an internal standard. Decoupling experiments were performed for some samples at 300 MHz using single-frequency, low-power, on-resonance conditions to remove the target absorption. A ^{13}C NMR spectrum was recorded for compound **22** at 125 MHz on the GN-500 instrument and a chemical shift correlation map technique was utilized to correlate proton shifts with the carbon atoms in the skeleton. Infrared spectra were obtained from CS_2 solution using a Perkin-Elmer 580B IR spectrometer. The optical rotation of compound **22** was measured using a 0.3 ml cell in a Rudolph 70 polarmeter (O.C. Rudolph and Sons Inc., Caldwell, NJ).

The following authentic standards were obtained commercially: (*E*)-2-hexenal and (*E*)-2-octenal (Bedoukian Research, Danbury, CT); carenes (Parks Corp., Somerset, MA); ocimenes (IFF, Union Beach, NJ); terpinolene and γ-terpinene (Roth, Plainview, NJ); phellandrenes (Givaudan, Clifton, NJ); sabinene, β-pinene, myrcene, limonene, linalool, terpine-4-ol and 2-phenylethanol (Aldrich Chemical, Milwaukee, WI). The following standards were synthesized according to published procedures: 4-oxo-(*E*)-2-hexenal [39], 8-hydroxylinalool (40], and the (*R,R/S,S*) and (*R,S/S,R*) pairs of racemates of 5-hydroxy-4-decanolide [41]. Identifications are primarily based on GC-MS data and GC coinjection.

(E)-2-*Hexenal* (**1**). MS *m/z* (%): 98([M]$^+$, 10), 83(28), 69(42), 57(33), 55(54), 40(57), 41(100) and 39(75).

4-*oxo*-(E)-2-*Hexenal* (**2**). MS *m/z* (%): 112([M]$^+$, 13), 84(13), 83(100), 69(1), 57(19), 56(9), 55(66), 53(8), 42(4) and 39(10).

(E)-2-*Octenal* (**3**). MS *m/z* (%): 111(12), 108(2), 97(7), 83(28), 70(49), 57(38), 55(65), 41(100) and 39(54).

4-*oxo*-(E)-2-*Octenal* (**4**). MS *m/z* (%): 140([M]$^+$, 1), 125(8), 111(57), 98(59), 83(58), 70(30), 57(33), 55(100), 41(70) and 39(40). An authentic standard was unavailable for this component, therefore identification of this widespread heteropteran exocrine compound [5] is based on comparison to a published spectrum [42] and analogy to the EI ionization of **1**.

3-*Carene* (3,7,7-*trimethyl-bicyclo*[4.1.0]*hept*-3-*ene*) (**5**). MS *m/z* (%): 136([M]$^+$, 8), 121(7), 105(6), 93(100), 92(35), 91(32), 81(2), 80(8), 79(19), 78(3), 77(25), 67(8), 53(10), 41(28) and 39(23).

4-*Carene* (3,7,7-*trimethyl-bicyclo*[4.1.0]*hept*-4-*ene*) (**6**). MS *m/z* (%): 136([M]$^+$, 19), 121(28), 107(2), 94(30), 93(100), 91(30),

81(31), 80(54), 79(69), 77(32), 69(18), 53(14), 43(22), 41(58) and 39(33). This insect-derived component coeluted with a minor component of the turpentine sample. A purer authentic standard was unavailable, therefore the identification is tentative.

Sabinene (*4-methylene-1-(methylethyl)-bicyclo*[3.1.0]*hexane*) (**7**). MS *m/z* (%): 136([M]$^+$, 14), 121(6), 107(2), 93(100), 91(30), 79(22), 77(29), 69(16), 65(5), 53(7), 43(10), 41(17) and 39(10).

β-*Pinene* (6,6-*dimethyl-2-methylene-bicyclo*[3.1.1]*heptane*) (**8**). MS *m/z* (%): 136([M]$^+$, 2), 121(2), 107(1), 93(58), 91(10), 79(9), 77(8), 69(56), 53(9), 41(100) and 39(20).

Myrcene (*7-methyl-3-methylene-1,6-octadiene*) (**9**). MS *m/z* (%): 136([M]$^+$, 2), 121(2), 107(1), 93(58), 79(9), 77(8), 69(56), 53(9), 41(100) and 39(20).

β-*Phellandrene* (3-*methylene-6-(1-methylethyl)*-cyclohexene) (**10**). MS *m/z* (%): 136([M]$^+$, 17), 121(3), 93(100), 91(31), 80(8), 79(17), 77(29), 69(4), 65(5), 53(4), 44(6) and 41(17).

Limonene (1-*methyl-4-(1-methylethenyl)-cyclohexene*) (**11**). MS *m/z* (%): 136([M]$^+$, 18), 121(16), 107(15), 93(53), 79(26), 77(14), 68(100), 67(78), 53(27), 41(34) and 39(41).

trans-β-*Ocimene*((E)-3,7-*dimethyl-1,3,6-octatriene*) (**12**). MS *m/z* (%): 136([M]$^+$, 8), 121(13), 105(14), 93(100), 92(25), 91(42), 80(41), 79(46), 77(34), 67(14), 55(16), 53(23), 43(33) and 41(58).

γ-*Terpinene* (1-methyl-4-(1-*methylethyl*)-1,4-*cyclohexadiene*) (**13**). MS *m/z* (%): 136([M]$^+$, 33), 121(25), 107(6), 105(8), 93(100), 91(42), 79(18), 77(35), 65(9), 53(8), 43(14) and 41(30).

Terpinolene (1-*methyl-4-(1-methylethylidene)-cyclohexene*) (**14**). MS *m/z* (%): 136([M]$^+$, 76), 121(78), 107(10), 105(15), 93(100), 91(39), 79(37), 77(34), 67(12), 65(10), 55(10), 53(19), 51(10) and 41(40).

2-*Phenylethanol* (**15**). MS *m/z* (%): 122([M]$^+$, 28), 92(57), 91(100), 77(5), 65(19), 51(9) and 40(15).

cis-*8-Hydroxylinalool*(2,6-*dimethyl*-(Z)-2,7-*octadiene*-1,6-*diol*) (**16**). Isobutane CI-MS *m/z* (%): 171([M+H]$^+$, 4), 153([M+H−H_2O]$^+$, 100) and 135([M+H−2H_2O]$^+$, 93); NH_3 CI-MS: 205([M+$(NH_3)_2$H]$^+$, 18), 188([M+NH_4]$^+$, 100) and 170([M+H]$^+$, 14); ND_3 CI-MS: 214([M+$(ND_3)_2$D−2H+2D]$^+$, 13) and 194([M+ND_4−2H+2D]$^+$, 100). EI-MS *m/z* (%): 152(1), 137(5), 119(11), 110(8), 109(6), 105(3), 96(10), 93(11), 84(36), 82(25), 81(20), 79(18), 71(100), 68(35), 67(82) and 55(55).

trans-8-*Hydroxylinalool*(2,6-*dimethyl*-(E)-2,7-*octadiene*-1,6-*diol*) (**17**). EI-MS *m/z* (%): 152(12), 137(9), 119(10), 110(12), 109(8), 105(4), 96(14), 93(16), 84(16), 82(25), 79(20), 71(100), 68(38), 67(82) and 55(59); lit. [43]: 152(5), 137(18), 119(13), 110(19), 93(20), 82(35), 71(100), 67(72), 55(35) and 43(84). CI-MS *m/z* (%) isobutane lit. [44]: 153([M+H−H_2O]$^+$, 33) and 135([M+H−2H_2O]$^+$, 100).

Perilla alcohol (4-(1-*methylethenyl*)-1-*cyclohexene*-1-*methanol*) (**18**). MS *m/z* (%): 152([M]$^+$, 8), 134(8), 121(56), 108(21), 93(60), 79(93), 68(100), 67(94) and 55(65). Identified previously from *N. louisianica* adults [4]; *N. louisianica* nymphal anterior DAG component **18** matched the MS and GC retention time of **18** from adults.

Thymol (2-*methyl*-5-(1-*methylethyl*)-*phenol*) (**19**). Identified previously [4].

Linalool (3,7-*dimethyl*-1,6-*octadien*-3-ol) (**20**). MS *m/z* (%): 154([M]$^+$, 1), 136(29), 121(67), 109(25), 93(65), 80(33), 71(100) and 55(63).

Terpinen-4-ol (4-*methyl*-1-(1-*methylethyl*)-3-cyclohexen-1-*ol*) (**21**). MS *m/z* (%): 154([M]$^+$, 10), 136(8), 111(42), 93(39), 86(21), 71(100) and 55(25).

(4S,5S)-(+)-5-*Hydroxy-4-decanolide* (**22**). EI-MS *m/z* (%): 186([M]$^+$, trace), 115(3), 101(7), 86(100), 85(25), 83(23), 58(18) and 55(42); NH_3 CI-MS: 221([M+$(NH_3)_2$H]$^+$, 100) and 204([M+NH_4]$^+$, 48); ND_3 CI-MS: 229([M+$(ND_3)_2$D−H+D]$^+$, 100) and 209 ([M+ND_4−H+D]$^+$, 43); $^{15}NH_3$ CI-MS: 223([M+$(^{15}NH_3)_2$H]$^+$, 100) and 205 ([M+$^{15}NH_4$]$^+$, 40). IR (CS_2) cm^{-1}: ν*C*=O 1791; IR($CDCl_3$) cm^{-1} lit. [32]: 1782. ^{1}H NMR (300 MHz, C_6D_6) δ 0.892 (3H, *t*), 1.09−1.36 (10H, *m*), 1.80 (1H, *ddd*), 2.02 (1H, *ddd*), 2.93 (1H, *m*), 3.63 (1H, *dt*) and 4.26 (1H, *s*). ^{13}C NMR (125 MHz, C_6D_6) δ175.4 (C-1), 28.40 (C-2), 22.95 (C-3), 82.08 (C-4), 73.40 (C-5), 33.13 (C-6), 25.46 (C-7), 31.99 (C-8), 23.80 (C-9) and 14.25 (C-10); lit. (25 MHz, C_6D_6) [32]: δ177.53 (C-1), 28.68 (C-2), 24.09 (C-3), 83.02 (C-4), 73.05 (C-5), 32.29 (C-6), 25.69 (C-7), 32.15 (C-8), 23.03 (C-9) and 14.31 (C-10). $[\alpha]_D^{23}$=+29.4° (*c* 0.05, $CHCl_3$; lit. $[\alpha]_D^{20}$=+33.2° (*c* 1.11, $CHCl_3$) [45]. The isolated natural product coeluted by GC with a mixture of synthetic (4*S*,5*S*)-/(4*R*,5*R*)-5-hydroxy-4-decanolide (R_t 4.9 min; 15 m DB-1, 125°C), but not with a synthetic (4*R*,5*S*)-/(4*S*,5*R*)-5-hydroxy-4-decanolide mixture (R_t 5.3 min).

Boxelder bugs were collected in Anne Arundel County, Maryland, and near Salt Lake City, Utah. *Boisea rubrolineatus* adults were collected on the campus of the University of California, Berkeley. *Jadera haematoloma* larvae and adults were collected in Fort Meyers and Plantation Key, Florida; Patagonia, Arizona; and Woodward and Norman, Oklahoma. *Jadera sanguinolenta* were collected in Miami, Florida. Adults of *J. antica* were collected at Plantation Key, Florida, the adult male *J. obscura* was collected at Barro Colorado Island, Panama, and the adult male *J. hinnulea* was collected in the lower Rio Grand Valley, Texas.

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